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(54) **Process for preparing 1-chloro-2,2,2-trifluoroethane.**

(57) 1-Chloro-2,2,2-trifluoroethane is prepared in a good yield and good selectivity by fluorinating trichloroethylene with hydrogen fluoride in the presence of a compound of the formula:

$SbCl_xF_y$

wherein x and y are both a positive number and the sum of x and y is 5, wherein an amount of hydrogen fluoride in a reaction system is at least five moles per one mole of the catalyst.

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## BACKGROUND OF THE INVENTION

### Field of the Invention

The present invention relates to a process for preparing 1-chloro-2,2,2-trifluoroethane (hereinafter referred to as R-133a). R-133a as such is useful as an intermediate in the preparation of a pharmaceutical or agricultural compound, and is fluorinated with anhydrous hydrogen fluoride to give to tetrafluoroethane which acts as a working fluid.

### Description of the Related Art

It is known that R-133a is synthesized by contacting trichloroethylene and hydrogen fluoride (HF) to a catalyst compound of the formula:

$SbCl_xF_y$

wherein x and y are both a positive number and the sum of x and y is 5. However, by this synthesis process, a large amount of chlorides are by-produced and Sb in the catalyst is deteriorated to a trivalent metal. To reactivate the deteriorated catalyst, chlorine ($Cl_2$) is introduced in a reaction system. Therefore, both a yield and a selectivity are very low, and this process is not an industrial process which can produce R-133a easily at a low cost (see U.S. Patent No. 3,003,003).

In a conventional process disclosed in Japanese Patent Kokai publication No. 135909/1978, a large excess amount of HF is used in the synthesis of R-133a. However, only about 50 % of HF is utilized. When an exceeding amount of HF is diminished in this process, the selectivity greatly decreases. Since this process is a batchwise process so that an operating efficiency of an apparatus is low when it is carried out in an industrial scale, it is not easily operable process.

## SUMMARY OF THE PRESENT INVENTION

One object of the present invention is to provide a process for preparing R-133a in a good yield and selectivity.

Another object of the present invention is to provide a process for preparing R-133a economically in an industrial scale.

According to the present invention, there is provided a process for preparing R-133a comprising fluorinating trichloroethylene with hydrogen fluoride in the presence of a compound of the formula:

$SbCl_xF_y$

wherein x and y are both a positive number and the sum of x and y is 5, wherein an amount of hydrogen fluoride in a reaction system is at least five moles per one mole of the catalyst.

## DETAILED DESCRIPTION OF THE INVENTION

In a preferred embodiment, the fluorination is carried out by introducing trichloroethylene and hydrogen fluoride in the reaction system and recovering R-133a from the reaction system while keeping a reaction pressure constant.

Preferably, a molar ratio of HF to trichloroethylene is at least 4:1, and prepared R-133a is recovered from the reaction system as an azeotropic mixture with HF.

While trichloroethylene is cheap and desirable as a starting material, in addition to or in place of trichloroethylene, 1,2,2-trichloro-2-fluoroethane or 1,2-dichloro-2,2-difluoroethane may be used as a starting material. 1,2,2-Trichloro-2-fluoroethane or 1,2-dichloro-2,2-difluoroethane is an intermediate of the above fluorination reaction, and it does not interfere with the fluorination reaction. Since the addition reaction of HF to trichloroethylene and fluorination of 1,2,2-trichloro-2-fluoroethane or 1,2-dichloro-2,2-difluoroethane proceed successively, they may be carried out in series.

An amount of HF is usually from 5 to 500 moles, preferably from 50 to 300 moles per one mole of the $SbCl_xF_y$ catalyst. When the amount of HF is larger than the above upper limit, a productivity per a unit volume of a reactor decreases, although the reaction itself is not influenced. When the amount of HF is smaller than the above lower limit, though the reaction proceeds, an amount of trichloroethylene to be introduced should be decreased so as to avoid decrease of the selectivity, and efficiency is deteriorated.

The amount of HF is at least a total amount of HF which is consumed in the reaction and HF which forms the azeotropic mixture. When the amount of introduced HF is too large, the productivity of R-133a undesirably decreases, and a utilization factor of HF decreases, since the amount of HF in the reaction system is kept constant. Preferably, the amount of introduced HF is from 4 to 8 moles per one mole of trichloroethylene, from 3 to 6 moles per one mole of 1,2,2-trichloro-2-fluoroethane, or from 2 to 4 moles per one mole of 1,2-dichloro-2,2-difluoroethane.

An amount of trichloroethylene to be introduced in the reactor is 5 to 100 mol/hour, preferably from 10 to 50 mol/hour per one mole of the $SbCl_xF_y$ catalyst. When the amount of trichloroethylene is too small, the productivity decreases although the reaction proceeds. When the amount of trichloroethylene is too large, the content of fluorine in the $SbCl_xF_y$ catalyst decreases so that

the selectivity decreases though the reaction proceeds.

The reaction is carried out at a temperature of 30°C or higher. At a temperature slightly higher than 30°C, the selectivity decreases if the amount of introduced trichloroethylene is not small in relation to the amount of the $SbCl_xF_y$ catalyst. Increase of the reaction temperature may be favorable for the productivity and the selectivity, but at high reaction temperature, a reaction pressure should be kept high. Since the high reaction pressure increases a cost of an equipment, practically the reaction temperature is from 50 to 150°C.

The reaction pressures is selected from a range between 3 and 30 kg/cm$^2$ so as to separate R-133a from HF by increasing the pressure as the temperature is raised. It is possible to accumulate R-133a in the reaction system by the increase of reaction pressure while removing by-produced HCl from the reaction system.

To have the $SbCl_xF_y$ catalyst present in the reaction system, it is preferred to add antimony pentachloride to the reaction system.

It is known that added antimony pentachloride is partly fluorinated with HF to form $SbCl_xF_y$. When $SbCl_xF_y$ is used as a catalyst for the fluorination of a compound having a hydrogen atom which can be chlorinated or a double bond such as trichloroethylene, the fluorination reaction rate increases as the content of fluorine in $SbCl_xF_y$ increases, whereby side reactions are suppressed.

By using the excess amount of HF in relation to antimony pentachloride to keep the fluorine content in $SbCl_xF_y$ high, an addition reaction is promoted and in turn R-133a is produced with a good selectivity. That is, by regenerating consumed $SbCl_xF_y$ having the high fluorine content with the excess amount of HF and supplying trichloroethylene at a rate which does not exceed a regeneration rate of the catalyst, the fluorine content in $SbCl_xF_y$ is kept high and the production of R-122, which tends to be formed when the chlorine content in $SbCl_xF_y$ is high, is suppressed.

By the presence of excessive HF, the addition reaction of HF to the olefin, which is a competitive reaction with chlorination, proceeds quickly.

By the process of the present invention, R-133a is prepared with a good selectivity and deterioration of $SbCl_xF_y$ caused by chlorination can be suppressed.

## PREFERRED EMBODIMENTS OF THE INVENTION

The present invention will be illustrated by the following Examples.

### Example 1

In a 500 ml autoclave, $SbCl_5$ (10 ml, 0.05 mol) was charged and cooled with dry ice, and then HF (100 ml) was introduced. After an internal temperature of the autoclave rose to room temperature, the mixture was heated at 50°C for 2 hours and then at 60°C for 6 hours, while vigorously stirring. Thereafter, in the mixture, trichloroethylene and HF were introduced at rates of 0.25 mol/hour and 1 mol/hour, respectively. The product was withdrawn from the autoclave through a cooling tube to keep the reaction pressure at 6.2 kg/cm$^2$. After carrying out the reaction for 8 hours and when 2 moles of trichloroethylene were supplied, the reaction was terminated, and organic materials collected in a dry ice-cooled trap were analyzed. The results are as follows:

Yield: 180 g

GLC analysis (TCD):

R-133a:
93.1 %

R-132b (1,2-dichloro-1,1-difluoroethane):
3.4 %

R-122 (1,2,2-trichloro-1,1-difluoroethane):
3.3 %

The organic materials in the autoclave were also analyzed to find that the total yield of R-133a was 92 %.

### Example 2

In a 500 ml autoclave, $SbCl_5$ (10 ml, 0.05 mol) was charged and cooled with dry ice, and then HF (100 ml) was introduced. After an internal temperature of the autoclave rose to room temperature, the mixture was heated at 50°C for 2 hours and then at 60°C for 6 hours, while vigorously stirring. Thereafter, the internal temperature was further raised to 80°C and, in the mixture, trichloroethylene and HF were introduced at rates of 0.5 mol/hour and 2 mol/hour, respectively. The product was withdrawn from the autoclave through a cooling tube to keep the reaction pressure at 8.5 kg/cm$^2$. After carrying out the reaction for 4 hours and when 2 moles of trichloroethylene were supplied, the reaction was terminated, and organic materials collected in a dry ice-cooled trap were analyzed. The results are as follows:

Yield: 194 g

GLC analysis (TCD):

| | |
|---|---|
| R-133a: | 97.5 % |
| R-132b: | 2.4 % |
| R-122: | 0.5 % |

The organic materials in the autoclave were also analyzed to find that the total yield of R-133a was 96 %.

### Example 3

In a 500 ml autoclave, $SbCl_5$ (10 ml, 0.05 mol) was charged and cooled with dry ice, and then HF (200 ml) was introduced. After an internal temperature of the autoclave rose to room temperature, the mixture was heated at 50 °C for 2 hours and then at 60 °C for 6 hours, while vigorously stirring. Thereafter, the internal temperature was further raised to 80 °C and, in the mixture, trichloroethylene and HF were introduced at rates of 0.5 mol/hour and 2 mol/hour, respectively. To keep the reaction pressure at 8.5 kg/cm$^2$, the autoclave was cooled by circulating a cooling water of 60 °C and the product was withdrawn from the autoclave through a cooling tube. After carrying out the reaction for 4 hours and when 2 moles of trichloroethylene were supplied, the reaction was terminated, and organic materials collected in a dry ice-cooled trap were analyzed. The results are as follows:

Yield: 207 g

GLC analysis (TCD):

| | |
|---|---|
| R-133a: | 97.6 % |
| R-132b: | 2.3 % |
| R-122: | <0.1 % |

The organic materials in the autoclave were also analyzed to find that the total yield of R-133a was 97 %.

## Example 4

In the same manner as in Example 3 but circulating a cooling water of 40 °C, the reaction was carried out. The results are as follows:

Yield: 185 g

GLC analysis (TCD):

| | |
|---|---|
| R-133a: | 99.8 % |
| R-132b: | 0.2 % |

The organic materials in the autoclave were also analyzed to find that the total yield of R-133a was 97 %.

As seen from the results of Example 4, the purity of the product depends on an efficiency of the cooling tube and the number of plates. Therefore, contamination of the product with the intermediates such as 132b can be prevented easily by the present invention.

## Claims

1. A process for preparing 1-chloro-2,2,2-trifluoroethane comprising fluorinating trichloroethylene with hydrogen fluoride in the presence of a compound of the formula:

   $SbCl_xF_y$

   wherein x and y are both a positive number and the sum of x and y is 5, wherein an amount of hydrogen fluoride in a reaction system is at least five moles per one mole of the catalyst.

2. The process according to claim 1, wherein trichloroethylene and hydrogen fluoride are introduced in a reaction system and 1-chloro-2,2,2-trifluoroethane is recovered from the reaction system while keeping a reaction pressure constant.

3. The process according to claim 1, wherein a molar ratio of hydrogen fluoride to trifluoroethylene is at least 4:1.

4. The process according to claim 3, wherein said molar ratio of hydrogen fluoride to trifluoroethylene is from 4:1 to 8:1.

5. The process according to claim 2, wherein 1-chloro-2,2,2-trifluoroethane is recovered as an azeotropic mixture with hydrogen fluoride.

6. The process according to claim 1, wherein an amount of hydrogen fluoride is from 5 to 500 moles per one mole of $SbCl_xF_y$.

7. The process according to claim 1, wherein a reaction temperature is at least 30 °C.

8. The process according to claim 1, wherein a reaction pressure is from 3 to 30 kg/cm$^2$.

9. The process according to claim 1, wherein antimony pentachloride is added to the reaction system.

10. The process according to claim 1, wherein 1,2,2-trichloro-2-fluoroethane or 1,2-dichloro-2,2-difluoroethane is added to the reaction system.

European Patent Office

# EUROPEAN SEARCH REPORT

Application Number

EP 91 10 9749

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Cl.5) |
|---|---|---|---|
| X | FR-A-2 388 785 (BAYER)<br>* Examples; claims<br>* & JP-A-53 135 909 (Cat. D)<br>– – – | 1,3-4,6 | C 07 C 19/08<br>C 07 C 17/00 |
| A,D | US-A-3 003 003 (R.L. McGINTY)<br>– – – – – | | |
| | | | TECHNICAL FIELDS SEARCHED (Int. Cl.5) |
| | | | C 07 C 17/00 |

The present search report has been drawn up for all claims

| Place of search | Date of completion of search | Examiner |
|---|---|---|
| The Hague | 23 September 91 | VAN GEYT J.J.A. |

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same catagory
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention

E: earlier patent document, but published on, or after the filing date
D: document cited in the application
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